A STUDY OF SOME OF THE SALTS OF PHYTIC ACID

BY

PETER GEORGE ARVAN

B.S., University of Illinois, 1943
A.M., Indiana University, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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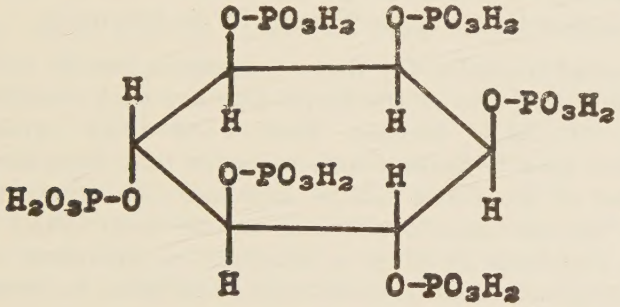
Introduction

Phytic acid has been shown to be a hexaphosphoric acid ester of inositol (1,2). As a derivative of inositol there are eight possible geometrical isomers. Investigations have shown that phytic acid has the following stereochemical structure (3):



When sodium phytate acts as a coordinating agent, it is possible for it to complex more than one metal ion. Adjacent $(-O-PO_3)^=$ groups in the phytate group may function as bidentate and possibly as polydentate units. There is some doubt, however, as to whether adjacent $(-O-PO_3)^=$ groups, which are on the same side of the plane of the ring, can function as polydentate units. The distance between two such $(-O-PO_3)^=$ groups is not much more than the distance across one carbon tetrahedron. It is doubtful, therefore, that there would be room for a metal ion to fit into a chelate structure which would form if two *cis* $(-O-PO_3)^=$ groups function as a unit. It seems more plausible to suppose that adjacent $(-O-PO_3)^=$ groups which are on opposite sides of the plane of the ring may form a bidentate or polydentate unit. Further, the possibility of a single $(-O-PO_3)^=$ group acting as a monodentate unit or even as a polydentate unit cannot be excluded.

Theoretical And Discussion Of Results

The structure of the complex compounds prepared by Otolski (4) can be explained on the basis of the above theory. Otolski found that the reaction of water insoluble tetraferric phytate with various monodentate and bidentate amines gave water soluble compounds which correspond to the general formulas $Fe_4(C_6H_6O_{24}P_6)\cdot 6MD$ and $Fe_4(C_6H_6O_{24}P_6)\cdot 4BD$, where MD and BD represent the mono- and bidentate amines, respectively. In each case the amine used is not capable of complexing the ferric ion by itself; because of its basic nature in aqueous solution, it precipitates ferric hydroxide.

Logical formulas for these compounds can be written by assuming that two of the ferric ions are each coordinated to two $(-O-PO_3)^=$ groups. Each $(-O-PO_3)^=$ group must function as a tridentate unit in order that the coordination number of the ferric ion be satisfied. The two remaining ferric ions are each coordinated to one $(-O-PO_3)^=$ group, which functions as either a bidentate or tridentate unit; the remaining coordination positions are satisfied by three monodentate amine molecules, or by two bidentate amine molecules.

A study of the cobaltous phytate complexes has shown that the phytate group can coordinate up to four cobaltous ions. The stability of these complexes is directly dependent on the pH of the medium in which they exist. The complexes in which the cobalt to phytate ratio is 4:1, 2:1, or 3:2 were found to decompose as the pH of the solution was lowered, decomposition beginning at 8.8, 8.6, and 8.1, respectively. The products formed on decomposition are cobaltous hydroxide and a mixture of the penta- and hexacobaltous phytate. When solutions in which the cobalt to phytate ratio is 1:1 or less, are used, they do not yield the above mentioned precipitate. The only observable change is the fading of the lavender color of the complex to the pink of the hydrated cobaltous ion.

It was concluded that the 1:1 complex is the only complex which is stable in solutions the pH of which is below seven. The experimental evidence further indicates that this complex

decomposes to the hydrated cobaltous ion and the phytate group $[C_6H_6O_{24}P_6H_z]^{(z-12)}$ where z is eight, when the pH of the solution is lowered to five.

When the cobaltous phytate complexes are titrated with sodium hydroxide, the color of the solution changes from lavender to blue, if the blue color was not present at the outset as in the solutions in which the cobalt to phytate ratio is 2:1 or greater. When the pH of the system reaches 11.5, the solutions become cloudy, and cobaltous hydroxide slowly begins to precipitate.

The cupric phytate complexes were studied polarographically (5), and a 1:1 complex was found to exist at the concentrations used. The half-wave potentials were measured in solutions which were 0.01 molar and 0.10 molar with respect to sodium phytate. In each case the cupric ion concentration was maintained constant at 5×10^{-4} molar. This study has shown that the reaction at the dropping mercury electrode is reversible, and the 1:1 complex is reduced to metallic copper (amalgam) without the intermediate formation of a cuprous complex. The half-wave potential in 0.10 molar phytate solution was found to be -0.207 volts as compared to $+0.016$ volts for the hydrated cupric ion in 0.10 molar potassium nitrate solution (6). The dissociation constant of the complex was found to be 2.8×10^{-8}. This complex is much less stable than the bis-ethylenediamine cupric complex, which has a dissociation constant of 2.1×10^{-20} (6).

Only limited titration studies of the cupric phytate complexes were possible due to the extreme insolubility of cupric hydroxide. This study has shown that the 1:1 complex is less stable towards acid than the corresponding cobaltous complex. As in the case of the cobaltous complexes, the insoluble metal hydroxide was formed when the pH of the solutions was increased to 11.5.

An attempt was made to study the zinc and cadmium complexes polarographically, but both reductions were found to be irreversible at the dropping mercury electrode. A

qualitative statement, however, may be made regarding the ease of reducibility of these complex ions. The potential at which the zinc complex begins to reduce is about —1.70 volts as compared with —1.50 volts for the $(ZnO_2)^=$ in one normal sodium hydroxide, and —1.01 volts for the hydrated zinc ion in one normal potassium nitrate solution (5). The potential at which the cadmium complex begins to reduce is —0.75 volts as compared to —0.59 volts for the hydrated cadmium ion in one normal potassium nitrate solution (5).

A study of the calcium phytate complexes has shown that the 1:1 complex is the only one which can be prepared in solution. All attempts to increase the calcium to phytate ratio resulted in the formation of an insoluble material, which analysis indicated to be $Ca_2Na_8C_6H_6O_{24}P_6 \cdot 3H_2O$ (7).

On standing, solutions in which the ratio of calcium to phytate was 1:1 or less also yielded precipitates which were shown to be the dicalcium octasodium phytate trihydrate.

The evidence appears to support the theory that the calcium ion is complexed by the phytate group. No precipitate of calcium carbonate or calcium oxalate is formed if a solution which contains both calcium ion and the phytate group is treated with a solution of sodium carbonate or sodium oxalate. Solutions of calcium ion alone, with the pH adjusted to the same value as in the case in which phytate is used, give immediate precipitates with sodium carbonate or sodium oxalate.

This study has shown that the phytate group is an excellent complexing agent in basic solution. Under the proper conditions, it may complex unusually large amounts of metal ions, as demonstrated in the case of cobaltous ion. Some preliminary tests have shown that this material may be of value as a sequestering agent to be used in metal plating baths.

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VITA

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He is a joint author of the following publications:

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